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Some Halogen Substitution Products  
of Benzene Sulphide.

Dissertation

presented for the degree of Doctor of  
Philosophy to the Board of University  
Studies of the Johns Hopkins University

by.  
Rudolf de Rode.

1890.

54-343.

## Note of Acknowledgement

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Rudolf de Rooder.



## Part II. Experiments.

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### Introduction

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Para-chlor-toluene-ortho-sulphonic acid	-
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Para-iodo-toluene-ortho-sulphonic acid	5
Para-chlor-toluene-ortho-sulphon-amide	20
Para-chlor-toluene-ortho-sulphon-amide	25
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## Introduction.

In a paper published in the American Chemical Journal No. 9, 822 Remond and Barley describe a method of preparation and the properties of para-brom-nitro-benzoic acid. Its most characteristic property was that it possessed two opposite and distinct tastes, a sweet and a bitter. The substance was made the subject of an investigation by Drs. Howell and Castle of the Johns Hopkins University, and in a paper entitled "On the Nerves of Taste" it was shown by them that the nerves in the tip of the tongue are of a different character from those in the back part of the



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longue, and that on the tip of the tongue the substance is only sweet while on the back part of the tongue it is only bitter.

Mc Castle of the John Hopkins University also prepared para-chlor-nitro-quinuclidine, in order to ascertain if it had a similar effect upon the nerves of taste. It was found to possess both tastes in a more marked degree than did para-nitro-quinuclidine.

The object of this research was to investigate the other para-halogens-quinuclidines, and the substances from which they were made and to observe their effect upon the nerves of taste. It was thought that some definite relation might be found to exist between the intensity of the taste and the chemical nature of the substances contained in the sulph.



imile. Since para-fluor-sulphide was both sweet and bitter, and para-chlor-sulphide was more sweet and more bitter it seemed probable that para-fluor-sulphide would be still more sweet & still more bitter while para-iodo-sulphide would not be either as sweet or as bitter as the para-sulphide we would thus have a series running thus.

Para-fluor-sulphide	=	Sweet.	Bitter
.. chlor	..	Sweet.	Bitter
.. brom	..	Sweet.	Bitter
.. iodo	..	Sweet.	Bitter

As regards this point, however, it may be at once stated that no such ~~as~~ delicate relation was found to exist; for para-fluor-sulphide was almost purely sweet with as sweet as sucrose sulphide, with only a very slight bitter after-taste; and para-iodo-sulph-



imide had very little taste at all and that was purely bitter; so that the series would run thus:

Para- -thio- -sulphoxide	SWEET	bitter
" chlor	Sweet	Bitter
" brom	Sweet	Bitter
" iodo	—	bitter

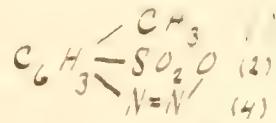
It appears obvious that no definite relation exists between the structure, or chemical activity, of the substituted halides and the taste of the corresponding sulphides.

The diazo compound which formed the starting point in these investigations, was made by starting with para-nitro-benzoic acid, converting this into the ortho-sulphonic acid which by reduction with tin and hydrochloric acid passed over into para-benzoic-sulphonic acid from which the diazo compound was made.



Paraffin to urea with sulphuric acid

The character point in the preparation of the various compounds described in this paper was para-urea-sulphuric acid" of the formula



This was made in the following manner: 50 grams of finely powdered para-bromine-sulphuric acid<sup>(2)</sup> were made into a thin paste with 75 c.c. of water in a 500 c.c. flask. The flask was placed in a bath of ice-water, and a rapid current of the gas from nitric acid and arsenic trioxide passed into it. The flask being constantly agitated in from 3 to 5 minutes the contents of the flask had a

(1). Ascher. Ann. Chem. 161, 8.

(2). Brackett and Hayes. Am. Chem. Soc. Trans. 9, 400



fully saturated and granular  
 crystals of the diazo compound had  
 separated out. The current of gas was  
 then stopped and the diazo compound  
 almost completely precipitated as a  
 heavy, granular mass, by the addition  
 of about 30ccs of alcohol. After stand-  
 ing for a few minutes, the contents  
 of the flask were thrown on a filter  
 covered with a funnel washed with  
 alcohol then with ether, and dried.  
 In this manner, from 50 grams of para-  
 toluidine-sulphonic acid, 42 grams of pure  
 white diazo-toluene-sulphonic acid were  
 obtained.

I. .3973 gr gave .0555 gr nitrogen

II. 3336 .. .. 0468 ..

Calculated for

$C_7H_6O_2N_2S$

Nitrogen = 14.14%

Found

I II

13.97% 14.03%



## Para-Fluorobenzoic- $\alpha$ -nitro-sulfuric acid.

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This acid was prepared by decomposing para-nitro-nitro-sulfuric acid with hydrofluoric acid in the following manner:

About 500 c.c. of concentrated hydrofluoric acid were slowly warmed in a large platinum dish and 20 grams of the dry compound dissolved in it. The dry compounds dissolved very readily. The solution was heated until decomposition, accompanied by evolution of nitrogen, began. The decomposition was allowed to take place slowly, and when complete the contents of the dish were evaporated to a mucous consistency, diluted with about two liters of water in a large porcelain



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dish heated, neutralized with pre-  
cipitated chalk, boiled with animal  
charcoal and filtered. The filtered  
solution gave a blue color with ferric  
chloride owing to the fact that some  
of the diazo-compound had been con-  
verted into para-phenol-sulfuric acid  
by the action of the water of the hy-  
drochloric acid solution. The calcium  
salt of the para-fluor-benzen-sulfuric  
acid was not obtained well crystallized,  
and sufficiently pure for analysis. The  
barium salt, however, (obtained by  
neutralizing with barium carbonate  
instead of precipitated chalk) was ob-  
tained in a very pure condition in  
small glistening scales. It was recrys-  
tallized until its solution no longer  
gave a color with ferric chloride and  
was clear.



	600 or heated till constant weight lost .0235 gr.		
I { .5925 ..	dry salt gave .2704 gr. Ba SO <sub>4</sub>		
.592 ..	heated till constant weight lost .0037 gr.		
I { 1053 ..	dry salt gave .0477 gr. Ba SO <sub>4</sub>		
	Calculated for	Found	
	(C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> ST) <sub>2</sub> Ba + H <sub>2</sub> O	I	II
H <sub>2</sub> O =	3.38 %	3.81 %	3.40 %
Ba =	26.60 ..	26.83 ..	26.63 ..

As a qualitative test for fluorine, a small quantity of the salt was mixed with lime, & ignited in a platinum crucible, or fused with caustic potash in a silver crucible, dissolved in hydrochloric acid, (treated with a little calcium chloride if caustic potash has been used) & neutralized with ammonia. A precipitate of calcium fluoride was thus obtained, which when heated with sulphuric acid browned



an etching on a watch-glass. One of these tests was employed in all of the cases where fluorine compounds were made and fluorine was found to be present in all.

Potassium Fluor-Silicate-Sulphonate was made from the barium or calcium salt by heating with potassium carbonate. It crystallized from concentrated aqueous solution in large glistening scales. It is very soluble in water. It may be precipitated as a granular powder by adding alcohol to the concentrated aqueous solution. The salt contains two molecules of water of crystallization.

5.5 gm. heated till constant weight 6.8575 gms.

$\frac{6.8575}{5.5} \times 1000 = 125.55 \times 1000 = 125.55$

$125.55 \times 1000 = 125550 \times 1000 = 125.55$

$\frac{125.55}{5.5} \times 1000 = 227.36 \times 1000 = 227.36$



Calculated for $C_7H_6O_3SFR + 2H_2O$	$\Sigma$	Found $\Sigma$
$\pi_1 O = 13.62\%$	13.71%	13.57%
$R = 17.14\ldots$	17.05	17.19

It is evident that chlorine is present in excess.

### Para-chlor-benzen-sulphuric acid

This acid was made by decomposing chloro-benzen-sulphuric acid by hydro-chloric acid in the same manner in which the chlor-benzen-sulphuric acid was made. Concentrated hydro-chloric acid was used, and the product of decomposition was evaporated on the water bath until very little smell of hydrochloric acid remained.

The benzen acid was made in almost the same manner with the only difference that the water of hydrochloric acid was replaced with ammonia in order to decompose the chloro-benzen-sulphuric acid.



and praseoal titteries, and evapora-  
tion to dryness. The solution was  
as in the case of the decomposition  
with nitro-ferric acid and then  
evaporated until a white and  
precious salt. The solution gave a  
resol-sulfuric acid. The barium  
salt was washed with sulfuric acid  
separated out in wart-like, a-  
morphous, granular aggregates. It  
was recrystallized until its solution no  
longer gave a color with ferric chloride.  
The salt is very little more soluble in  
hot than in cold water. It contains  
one molecule of water of crystallization.

$\frac{1}{2} 2190$  gr. heated till constant wt. lost .007002.

$\frac{1}{2} 220$  .. dry salt wt. .0528 gr. BaS<sub>2</sub>.

$\frac{1}{2} 227$  - heated till constant wt. lost .007002.

$\frac{1}{2} 23500$  .. moist salt .0905 gr. BaS<sub>2</sub>



Calculated	Found	
$(C_7H_6O_3S\text{Cl})_2\text{Ba} \cdot n\text{H}_2\text{O}$	$\equiv$	$\equiv$
$\text{Ba} = 5.15\%$	$3.20\%$	$3.09\%$
$3\text{H}_2\text{O} = 25.0\%$	$2.2\%$	$2.5\%$

There was a decrease over that obtained by Gmelin and, however, and Picard<sup>(2)</sup>

Potassium-chlor-oleum-sulphonate was made from the barium salt by treatment with barium carbonate in concentrated aqueous solution in light-yellow masses without water of crystallization.

$\equiv .3191\text{ gr}$  gave  $.1139\text{ gr K}_2\text{SO}_4$

$\equiv .2220\text{ .. ..} .1725\text{ ..}$

Calculated for	Found	
$C_7H_6O_3S\text{ClK}$	$\equiv$	$\equiv$
$\text{K} = 5.25\%$	6.00	16.11



## Pearl-milk-toluene-sulphuric acid

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This acid was made by adding gradually 100 grains of diazo-toluene-sulphuric acid to 200 grains of hot concentrated hydrobromic acid, and continuing the heating until decomposition was complete.

The Barium Salt was prepared in exact-  
in the same manner as that of the  
corresponding chlor-acid. It corresponds  
to the barium salt prepared by Gossel,  
and Hieber and Post<sup>(2)</sup>. The solution gave  
the color reaction with ferric chloride show-  
ing that here also some cresol-sulphuric  
acid had been formed.

The Platinum Salt was made from  
the barium salt by treatment with



potassium carbonate. The salt was not deliquescent in nature and had been crystallized from concentrated aqueous solution in thin luminous scales.

210.5 gr. heated till constant weight lost 0.22 gr.

99.6 .. dry salt gave .0598 gr  $K_2SO_4$

Calculated for

		Found
$C_7H_6O_3S \cdot 3rK^+ \cdot H_2O$		
$H_2O$ =	5.86%	5.79%

$K$  = 13.50 .. 13.50 ..

### Di-*iso*-toluene-*ortho*-sulphonic acid.

This acid was made by decomposing diazo-toluene-sulphonic acid with hydriodic acid in the following manner: 50 grams of the diazo-compound were placed in a flask with 250 c.c. of absolute alcohol and 57.0 grams of concentrated hydriodic acid (57%) added.



in small pieces the zinc being  
first powdered and heated until the  
evolution of nitrogen was over, the  
contents of the vessel are gradually  
warmed in order to complete the de-  
composition and the zinc is then  
left. The residue was diluted with 5 or  
6 litres of water, heated, neutralized  
with lead oxide, and filtered while  
boiling hot.

The Lead Salt was very difficultly  
soluble and could not be easily  
separated from the excess of lead  
oxide, by repeated boiling with water.  
After boiling out the zinc with  
water, the residue was treated with a  
solution of potassium carbonate, which  
converted any undissolved lead salt  
into the potassium salt which is  
easily soluble. The hot solution of



The lead salt upon cooling, becomes covered with an iridescent scum of a gummy consistency. If, however the solution be evaporated to a small bulk this scum gradually becomes as the boiling is continued breaks up and falls to the bottom in heavy flakes which can easily be separated. The mother liquor upon further evaporation yielded another lead salt which was very soluble. These lead salts were not themselves further investigated, but were at once converted into potassium salts by treatment with Potassium carbonate. The Potassium Salt obtained from the precipitate soluble lead salt by treatment with potassium carbonate, crystallized from carbonated ammonium aqueous solution in transparent,



whitish-shaped crystals, corresponding to the potassium salt of the 3-iodo-toluene-sulphuric acid described by Flammar. The salt contained iodine as was proved by a qualitative test, and crystallized with one molecule of water of crystallization.

I.  $\left\{ \begin{array}{l} \text{320.0} \text{ heated till constant weight lost .005 gr.} \\ \text{309.1} \text{ dry salt gave .07 gr K. Iod.} \end{array} \right.$

II.  $\left\{ \begin{array}{l} \text{309.0} \text{ heated till constant weight lost .0150 gr.} \\ \text{293.} \text{ dry salt gave .0721 gr K. Iod.} \end{array} \right.$

	Calculated for $(C_7H_6O_3SIK) \cdot H_2O$	Found	
		I.	II.
$H_2O =$	5.08%	5.18%	5.14%
K =	11.61 ..	11.11 ..	11.03 ..

The other potassium salt was much more soluble, and crystallized from concentrated aqueous solution in thin flakes. The salt did not contain iodine. On analysis it



gave fineness corresponded to the potassium salt of formic-citric acid  
 285 .. heated till constant weight lost .032 gr.  
 = 1.555 .. dry salt gave .0631 gr.  $K_2SO_4$   
 286 .. heated till constant weight lost .0221 gr  
 = 1.20 .. dry salt gave .1090 gr.  $K_2SO_4$   
 Calculated for  $K_2SO_4$  Found

$$\begin{array}{ccc}
 c_1 \pi_1 \theta_3 s K + \pi_2 \theta & \equiv & \equiv \\
 \pi_2 \theta = & 7.89^{\circ} & 7.82^{\circ} \quad 7.7^{\circ} \\
 K = & 8.57^{\circ} & 8.19^{\circ} \quad 8.75^{\circ}
 \end{array}$$

The para-iodo-benzoic acid from which this salt was formed, was undoubtedly formed by the action of iodo-benzoic acid upon the para-iodo-benzenesulphonic acid. Thus:



Two hours time 69.20



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oxy acids increases as we pass from hydrochloric to hydroiodic acid.

The dry potassium salts of fluor-, chloro-, and iodo-benzen-sulphonic acids just obtained were heated in tube with phosphorus pentachloride and then with ammonia, thereby giving the sulphur-chlorides and -anides. The details were as follows:

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### Para-fluor-benzen-ortho-sulphon-amide.

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This was obtained by heating together in a dish 50 grams of anhydrous potassium fluor-benzen-sulphonate, and 100 grams of phosphorus pentachloride; action taking place spontaneously, the mixture becoming hot & fuming in a dense white smoke. A greater part of the phosphorus anhydride



and washing with cold water, the re-  
sulting residue was washed and  
stained as a slightly yellow viscous  
liquid was allowed to drop slowly in-  
to a dish containing about a litre of  
strong aqueous ammonia. At first a bright  
yellow color was shown but after being  
boiled up with a bubble & then went  
into solution. The solution was evaporated  
to dryness on a water-bath, the residue  
baked with about 200 c.c. of alcohol and a  
little animal charcoal, filtered and  
evaporated to crystallization. The mude  
crystallized from the moderately concentra-  
ted alcoholic solution in large transpar-  
ent, apparently orthorhombic, prisms  
terminated in stone-faces. It was  
soluble in alcohol and not soluble in  
ether with difficulty in cold water. From  
a aqueous solution it crystallized in



was 55° uncorrected.

The combustion analyses made of this nitride, as well as of the various other compounds described hereafter were made as follows:

A mixture of about 4 parts by weight of finely divided lead chromate, and 1 part by weight of red lead, after being thoroughly washed was sucked into a compact mass on a funnel with a pump. While still moist the mixture was divided into lumps about the size of a pea, which were then heated to redness in a porcelain crucible, in small portions.

During the heating, stirring, etc. some of the lumps are broken up. When hot the mixture has a dark-brown or black color which changes to a bright red on cooling in the air. The nitride after



and fine are broken up in a mortar and  
mixed about the size of sand which are  
separated by a sieve from the finer  
portions. The finer portions are powdered  
and used to mix with the substance  
to be analyzed. The tube is filled as  
follows:



A piece of reduced copper gauze is necessary  
whether the substance to be analyzed  
contains nitrogen or not. This is placed  
in front of an asbestos plug A. Behind  
this plug is placed the coarsely granular  
mixture to about two thirds the length  
of the tube. This is held in place by  
an asbestos plug B and may be left  
unchanged so long as the tube is  
fit for use. Having the tube thus filled



from A to B, the remainder is filled as follows.

About two inches of the finely powdered preparation is introduced behind the plug B up to C. The weighed substance is then introduced, and about two inches more of the fine powder placed behind it. The substance is then intimately mixed with the fine powder by shaking & turning the tube. The remainder of the tube is then filled with the coarse grains up to F, and a passage made along the whole length of the tube by tapping it on a flat surface. The tube is placed in the furnace, connected in front with the calcium chloride tube and behind with an apparatus containing pure, dry air (or oxygen). The clamp at C is closed tight, the tube heated red-hot from the front up nearly to B.



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The tube is then heated from behind towards until it is all red-hot. When the mixture containing the substance is reached the gas jets are turned on gradually. When the bubbles of gas begin to pass too slowly through the potash bulbs, another jet is turned on &c. When the tube has remained red-hot throughout its entire length for some time, and the gas has ceased to bubble through the potash bulbs, the apparatus is connected with an aspirator which is set in operation and, hence, air is drawn through the apparatus in streams at  $\alpha$ , by which the rapidity of the current of air can be regulated. The tube is allowed to cool slowly while about one litre of air is drawn through it. The weighed tubes & bulb are then disconnected, and the tube closed in front



and in connection with the mixture  
absorbed behind such solid.

The tube may be used a second time  
by removing everything up to the plug  
3 from behind putting in a fresh  
piece of copper: care is necessary and  
proceeds as before. The tube may be  
used so long as it is fit for use, with-  
out disturbing the portion between 4 and  
3. The advantage of the mixture of  
lead bromate and red lead in the  
granulated form, is this, that it does  
not fuse down in the tube and pre-  
sents a larger surface of action. It  
can be heated to a red heat, and pre-  
sents all of the advantages of the  
oxide where copper oxide can not be  
used. The method has been used with  
good results in other substances in  
the form of granules.



In this method of analysis the hydrochloric-sulfuric acid gives the following results:

I.	3137	g.	gave	5.003	gr.	$\text{CO}_2$	and	1242	gr.	$\text{H}_2\text{S}$
II.	2525	"	"	2.87	"	"	"	998	"	"
III.	152	"	"	1.87	"	nitrogen	(nitrate)	"	"	"
IV.	225	"	"	1.682	"	$\text{BaSO}_4$	(barium)	"	"	"
V.	3155	"	"	1.123	"	"	"	"	"	"
VI.	225	"	"	0.16	"	"	(barium)	31	"	"
VII.	152	"	"	2.355	"	"	"	"	"	"

A similar analysis was made on the following sample:

	Calculated for	Found						
		I	II	III	IV	V	VI	VII
$\text{C} =$	47.47%	44.28%	44.32%	—	—	—	—	—
$\text{H} =$	4.23 "	4.40 "	4.38 "	—	—	—	—	—
$\text{N} =$	7.41 "	—	—	7.33%	—	—	—	—
$\text{S} =$	16.93 "	—	—	—	16.44%	17.23%	17.03%	17.35%
$\text{F} =$	1.26 "	—	—	—	—	—	—	—
$\text{O} =$	16.93 "	—	—	—	—	—	—	—
		<u>00.00</u>						

(1) This analysis was made by Mr. T. B. Strohfeld of the C. & I.



## Picr-chlor-tetra-methoxy-anilide

This was <sup>made</sup> in exactly the same manner as the Fluor-toluene-sulphure-anide. It was easily soluble in alcohol and hot water soluble with difficulty in cold water. It did not crystallize well from alcohol. From hot aqueous solution it crystallized on cooling, in long white needles.

The melting point was  $45^{\circ}$  uncorrected. This amide corresponded to that of Keller. On analysis the following results were obtained:

I. 2819 gr. gave 4210 gr.  $\text{CO}_2$  and 1021 gr.  $\text{H}_2\text{O}$

II. 3021 .. .. 4518 .. .. 1077 .. ..

III. 5161 .. .. 0356 .. nitrogen (Kjeldahl)

IV. 4901 .. .. 0337 .. .. ( .. )

V. 4420 .. .. 4530 ..  $\text{BaSO}_4$  (Fenton)



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I	27.8	wt.	gave	30.5	wt.	BaSO <sub>4</sub>	(Pearson)			
VII.	34.56	..	..	23.92	..	AgCl	(Burning with lime)			
VIII.	73.87	..	..	30.31	..	..	( .. .. .. )			
Calculated for										Found
<chem>C6H8O2NSCl</chem>										I II III IV V VI VII VIII
C =	40.88	%		40.73%	40.79%	—%	—%	—%	—%	—%
H =	3.89	..		4.02	3.96	—	—	—	—	—
O =	15.57	..		—	—	—	—	—	—	—
N =	6.81	..		—	—	6.89	6.88	—	—	—
S =	5.57	..		—	—	—	—	5.45	5.3	—
Cl =	7.28	..		—	—	—	—	—	—	—
	111.00	..								

Barium-thiure-molibdate-anneal.

This was made from potassium-thiure-molibdate-molybdate in the same manner as the corresponding fluor- and chlor- anides. The anide agreed with that prepared by Gussen<sup>(1)</sup> & Kübler & Post<sup>(2)</sup>

Ann Chem 72 235

(1) ... .. 1169, 15



Potassium-iodo-toluene-sulphonamide.

---

This was made by rubbing together in a dish, 50 grains of anhydrous potassium iodo-toluene-sulphonate, and 100 grains of phosphorous pentachloride. Action took place spontaneously, the mixture becoming hot & viscous. The resulting sulphur-chloride, after driving off most of the phosphorus oxychloride and washing with cold water was obtained as a white solid. When this was added to about a litre of strong aqueous ammonia it did not all go into solution on boiling as did the corresponding hydrogen compounds, but it was all converted into the amide nevertheless. This amide is, therefore, not so solu-



the in ammonia at the corresponding  
amides of the chlor- & chlor- & bromo-  
acetic acids.

The contents of the flask were evaporated  
to dryness on the water bath,  
boiled with about 200 cc. of alcohol +  
a little animal charcoal, filtered,  
and evaporated to crystallization.  
From the concentrated alcoholic solution,  
the amide crystallized in fine white  
needles. It is ~~insoluble~~<sup>insoluble</sup> in water,  
only sparingly soluble in hot water,  
from which on cooling it crystallizes  
in white needles finer than those in  
alcoholic solution. The melting point was  
185° to 187° (uncorrected). The amide agreed  
with the amide of  $\beta$ -iodo-bromo-  
butyric acid prepared by Glascock.  
In many of the willow leaves  
were obtained.



I. 19.0 gr. gave 20.11 gr.  $\text{CO}_2$  and .0566 gr.  $\text{H}_2\text{O}$

II. 12.00 .. .. 12.43 .. .. .0658 .. ..

III. 15.02 .. .. 12.300 .. nitroso (nitro) (1)

IV. 20.80 .. .. 16.71 "  $\text{AgI}$  and .670 gr.  $\text{BaSO}_4$  (Carus)

V. 25.39 .. .. 20.06 .. .. 20.03 .. .. ( .. )

Calculated for

Found

C: 28.28% 28.71% 27.80% —% —% —%

H: 2.69 .. 3.29 .. 3.32 .. — .. — .. — ..

O: 11.78 .. — .. — .. — .. — .. — ..

N: 7.31 .. — .. — .. 4.67 .. — .. — ..

S: 11.78 .. — .. — .. — .. 0.82 .. 0.83 ..

I: —2.70 .. — .. — .. — .. —2.04 .. —2.70 ..

100.00

These mixtures, under other conditions  
by means of an alkaline solution  
of potassium permanganate, yielded  
respectively fluor- chlor- brom-  
and iodo- sulphide. The per-

(1) This analysis was made by Mr. C. E. Sannen



centage of sulphonide obtained was in all cases, considerably less than the theoretical yield, although the oxidation was conducted under a variety of conditions. The best conditions which were found for obtaining the greatest yield in the sulphonide were in the case of an ox. thus as follows.

First of all, the anide must be free from foreign substances, as a small amount of the impurities which are liable to occur in the preparation of the anide, greatly affects the result.

2.5 mm. of the anide and 8 mm. of caustic potash are dissolved in 2 litres of water, in a 3 litre flask. The flask is placed in a bath of brine water, and a concentrated con-



tion of 35 grams of potassium berman-  
ganate added a little at a time.  
The flask is kept in the bath of  
boiling water until all of the mer-  
ganate is used up, or only a  
slight pink color remains. This requires  
as a rule from 2 to 3 hours. A little  
alcohol is then added, and the contents  
of the flask filtered, the residue wash-  
ed with hot water, & the filtrate evapo-  
rated to about 75 c.c. while still warm.  
The sulphide, however, with some am-  
monium sulphide, is precipitated by the  
addition of strong hydrochloric acid. When  
cold, the contents of the dish are thrown  
on a filter sucking with a pump, &  
washed with a little cold water. In  
order to separate the ammonium sulphide  
from the sulphide, the mixture  
is boiled with water, neutralized



with precipitated chalk, filtered and allowed to cool, when the amide crystallizes out of the solution in long white needles, and is separated. The solution on further evaporation yields the calcium salt of the sulphonamide. The calcium salts of para-fluor-, para-chlor-, para-bromo-, and para-iodo-sulphonamide all crystallize from concentrated aqueous solution in radial groups of white needles. These salts have the same tastes as the sulphonamides themselves. In analysis the following results were obtained.

### Calcium salt of para-Fluor-sulphonamide

I { .1876 gr heated till constant weight lost .0439 gr.  
{ .1437 .. dry salt gave .0446 gr  $\text{CaSO}_4$



2037 gr. heated till constant weight lost 0.0560 gr.  
 II { 0.56 .. dry salt gave .0488 gr.  $\text{CaSO}_4$

	Calculated for	Found	
	$(\text{C}_7\text{H}_3\text{O}_3\text{NSF})_2\text{Ca} \cdot 7\frac{1}{2}\text{H}_2\text{O}$	I	II
$\text{H}_2\text{O} =$	23.48 %	23.40 %	23.37.5
Ca =	9.09 ..	9.13 ..	9.19 ..

### Barium salt of baro-ther-sulphamide

2514 gr. heated till constant weight lost. 0560 gr.  
 I { 0.95 .. dry salt gave .0553 gr.  $\text{CaSO}_4$   
 25.5 .. heated till constant weight lost. 056 .. gr.  
 II { 1.1954 .. dry salt gave .0565 gr.  $\text{CaSO}_4$

	Calculated for	Found	
	$(\text{C}_7\text{H}_3\text{O}_3\text{NSC})_2\text{Ca} \cdot 7\frac{1}{2}\text{H}_2\text{O}$	I	II
$\text{H}_2\text{O} =$	22.20 %	22.27 %	22.31 %
Ca =	8.0 ..	8.32 ..	8.50 ..



Lithium salt of guanidino-sulphuric acid

This salt was prepared by Remsen and Barker. It gave twice the reaction to the ammonium  $(C_2H_3O_3NSI)_2Ca + 7/2H_2O$

Lithium salt of guanidino-sulphuric acid

I { .2575 gr. heated till constant weight lost .0439 gr.

{ .2136 .. dry salt gave .0440 gr  $CaSO_4$

{ .2482 .. heated till constant weight lost .0422 gr.

II { .2060 .. dry salt gave .0421 gr  $CaSO_4$

Calculated for  $(C_2H_3O_3NSI)_2Ca + 7/2H_2O$  Found

	I	II
$H_2O$ :	17.07%	17.05% 17.00%
Ca:	6.10 ..	6.06 .. 6.0 ..

The sulphurides themselves were obtained as precipitates, by adding hydrochloric acid to



The following colors of these various calcium salts. They are all difficultly soluble in cold water, & still more so in hydrochloric acid.

### Para-Fluor-sulfurine

This was made from its calcium salt by precipitation with hydrochloric acid. It is moderately soluble in hot water, from which on cooling it recrystallizes in long white needles which break up on drying into granules. When crystallized slowly however it remains in small compact cubes. Its taste was almost purely sweet, but after remaining in the mouth for a few minutes, a slight after-taste was perceptible. However as could be judged, no sweetness was fully so sweet as that of Kusnic anchi-



was collected and was 222.250 gms.  
It was on white gypsum sand;

I. 5086 gm. gave 77.2 gm.  $\text{CO}_2$  and .007 gm.  $\text{H}_2\text{S}$

II. 3080 .. .. 61.53 .. .. 0.6 .. ..

III. 7873 .. .. 133.70 .. nitroben (Pearson)

IV. 5008 .. .. 132.7 .. .. ( .. )

I. 3400 .. .. 30.53 ..  $\text{BaSO}_4$  (Pearson)

IV. 1856 .. .. 20.6 .. .. ( .. )

— insoluble and insoluble in water of dilute  
hydrochloric acid

6.24 g. 15 F. = = = I I I

C = - - - - - 0.5 - - 0.0 - - - - - - - - - - -

— = - - - - - 2.2 - - 2.28 - - - - - - - - - - -

I = 23.51 .. - - - - - - - - - - - - - - - - - - -

1 = 5.0 - - - - - 0.87 .. 0.03 - - - - - - - - - - -

S = 5.2 -

F = 6.25 -

50.20



## Para-chlor-sulfonide.

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This was made from its calcium salt by precipitation with hydrochloric acid. It was not quite so soluble as para-chlor-sulfonide. It crystallized from hot aqueous solution, on cooling, in thin flat plates. The melting point was  $218^{\circ}$  (uncorrected). It had both a sweet and a bitter taste. Both tastes were very marked, but the bitter seemed to be the more intense of the two. This substance was prepared in small quantity by the faculty of the Johns Hopkins University, in order to ascertain its effect upon the nerves of taste. It was not further studied. I have obtained an analysis in the following manner.



I.	4416	at 0 ave	237 gr. $\text{CO}_2$	and 0.7900 at 72.0	
I.	507	"	832	"	0.72 "
I.	3,25	"	477	"	0.56 "
II.	1,000	"	610.8	nitrogen at 25° & 735 mm. (Dumas)	
I.	1,000	"	62	"	" 730 " ( " )
I.	1,000	"	61.5	"	" 73 " ( " )
I.	7.0	"	1.77500	"	(Carious)
I.	7.0	"	1.7748	"	" "
I.	5.0	"	0.5707	32.82	(Carious)
I.	3897	"	0.192	"	( " )
II	1,0,2,0	"	6732	as 22 (Burning with lime)	
I.	1,000	"	6603	" ( " " " )	
I.	2.0	"	2.4	"	(Carious) (5)

Mineralization

Found

	C. H. O <sub>3</sub> N S Cl	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
C =	38.62	38.50	38.57	38.52	-	-	-	-	-	-	-	-	-	-	
H =	1.84	1.81	1.90	1.99	-	-	-	-	-	-	-	-	-	-	
O =	22.07	-	-	-	-	-	-	-	-	-	-	-	-	-	
N =	6.44	-	-	-	6.60	6.7	6.52	6.35	6.40	-	-	-	-	-	
S =	-	-	-	-	-	-	-	-	-	77	79	-	-	-	
Cl =	6.32	-	-	-	-	-	-	-	-	-	-	16.25	0.33	0.37	

These analyses were made by Dr. A. M. Peter of the U. S. Geol. Surv.

Mr. C. H. Holmes of the S. C. U.

(5) This analysis was made by Mr. B. C. since



## Para-nitro-sulphuride

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This was made from its calcium salt by precipitation with hydrochloric acid. It was slightly less soluble than para-chlor-sulphuride. It agreed in all respects with that prepared by Remsen and Bayley<sup>11</sup>. It possessed both a sweet and a bitter taste, but in a less marked degree than para-chlor-sulphuride. The yield obtained by conducting the oxidation in the sulphur-annular under the benzene mentioned conditions, was larger than was obtained by Remsen and Bayley. The yield was 0 to 12 percent of the theoretical.

## Para-nitro-sulphuride

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This was obtained from its calcium salt



is precipitated with hydrochloric acid. It was the least soluble of the barium salts. It crystallized from hot aqua regia solution, or when the fine white needles. Its melting point was  $230^{\circ}$ - $232^{\circ}$  (uncorrected). Its taste was not ~~no marked~~ ~~any~~ sweet nor foul either with no sweet taste whatever. On analysis the following figures were obtained:

I. .3440 gr. gave .3441 gr. CO<sub>2</sub> and .0414 gr. H<sub>2</sub>O

II. .2627 .. 2632 .. .. .0324 .. ..

III. .2577 .. 2853 .. .. .. .0361 .. ..

I. .32 .. .0273 .. nitrogen (Kieldahl)

II. .33 .. .0309 .. .. (Kieldahl)

III. .31 .. .32 .. AgI and .38 gr BaSO<sub>4</sub> (Carus)

IV. .2327 .. .1776 .. .. .. .1769 .. .. ( .. )

Calc'd. --- Found

..... 185 .. I = = = I I I =

C = 27.15% 27.28% 27.35% 27.38% -% -% -% -%

H = 2.05% 1.84% 1.37% 1.0% .. ..



$\text{C} =$	555	
$\text{N} =$	555	250-260
$\text{S} =$	555	140-170
$\text{Z} =$	555	20-25

It is well known that by boiling with dilute hydrochloric acid benzoic sulphide is converted into the acid ammonium salt of ortho-phenylbenzoic acid. It was thought reasonable that by similar treatment the para-halogen-sulphides would behave in the same manner. This was found to be the case with para-chlor-sulphide. The other para-sulphides were not investigated in regard to this point. They would probably act in the same way. 5 grams of para-chlor-sulphide were



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boiled with twice hydrochloric acid  
for about an hour. The flask being  
connected with a reflux condenser, the  
boiling of the acid was then ab-  
sorbed to dryness, & heated on the water-  
bath until all smell of hydrochloric  
acid had disappeared. The residue  
was dissolved in water, in which it  
was easily soluble. The solution had  
no taste and on titration  
gave 20.5 ml. ammonia in accordance  
to the acid ammonium salt of ortho-  
sulpho-benzoic acid. It was shown  
by analysis to be the acid ammonium  
salt of para-chlor-ortho-sulpho-benzoic  
acid.

2.5372 gr. gave .0359 gr.  $\text{NH}_3$

2.532 .. .032 .. ..

Calculated for  $\text{C}_7\text{H}_5\text{NO}_3\text{S} \text{--} \frac{1000\text{H}_2\text{O}}{902\text{NH}_3}$

$$\text{NH}_3 = 6.7\%$$

$$\begin{array}{c} \text{= 6.65\%} \\ \text{= 6.5\%} \end{array}$$



## Conclusion

The relative degrees of sweetness and bitterness and of sourness can only be roughly measured. It is also impossible to make accurate comparison between a sweet and a bitter taste as regards the relative intensity of the two. There is also a difference of opinion amongst those who have tasted these substances. The majority, however, were of the opinion that the substances have the tastes described in the preceding pages. These may be summarized thus:

Para-Fluor-sulphuric acid	= Sweet	>	Sour
"	= Sweet	<	Bitter
"	= Sweet	<	Bitter
"	= —		Bitter



## Biographical Sketch

The author of this paper, David John Lewis de Rose, was born on August 2<sup>d</sup> 1857 in Madison County, Kentucky. He graduated as Bachelor of Science at the State College of Kentucky in June 1885 and obtained the degree of Master of Science at the same institution two years later. He was elected as President Chemist at the Kentucky Agricultural Experiment Station from December 1885 till September 1886, at which time he entered the Johns Hopkins University as a candidate for the degree of Doctor of Philosophy, with Chemistry and Mineralogy as the subject of study. He was appointed Lecturer



Assistant to Prof. Dewey in 1888,  
and Fellow in Chemistry in 1889.

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Johns Hopkins University, March 30, 1901













